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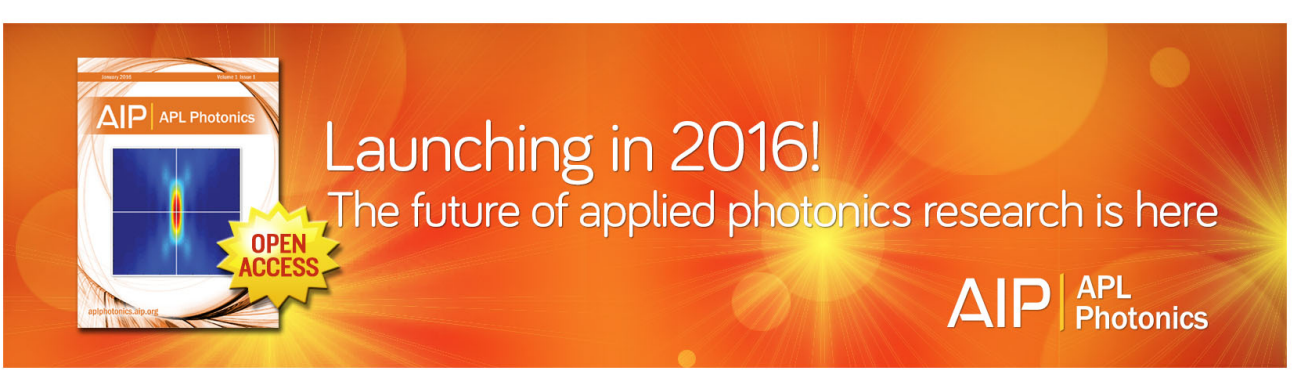

ESR spectra of PF_2 and SF_3 radicals*†

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Several years ago two of the present authors reported almost simultaneously the detection and identification of the radical PF_2 by ESR spectroscopy. Fessenden and Schuler[1] detected the radical during irradiation at −135 °C of nominally pure SF_6 with 2.8 MeV electrons, and found its spectrum to be considerably enhanced by the addition of small quantities of PF_3. Wan, Morton, and Bernstein,[2] on the other hand, detected the radical in γ-irradiated ND_4PF_6. The parameters describing this latter spectrum were $g = 2.0108 \pm 0.0002$, $a_P = 36.0 \pm 0.5$ G, and $a_F = 60.5 \pm 0.5$ G. In 1970, Wei, Current, and Gendell[3] also claimed to have observed the ESR spectrum of PF_2 formed by the thermal decomposition and photolysis of P_2F_4 and PF_2H. In spite of discrepancies in the g values, there was no suggestion that the earlier work[1,2] was suspect until Nelson, Jackel, and Gordy[4] obtained an isotropic spectrum of PF_2 by γ irradiation of PF_3 trapped in a xenon matrix. Their parameters were quite different from those of preceding workers, $g = 2.0020$, $a_P = 84.6$ G, and $a_F = 32.5$ G.

In order to resolve the issue we have sought new and unequivocal methods of preparing the radical PF_2: (a) The irradiation of 5 mole% PF_3 in a C_2F_6 matrix with 2.8 MeV electrons[5,6] and (b) The UV photolysis of PF_2Cl in the liquid phase.[7] Both of these methods were successful, and yielded ESR spectra of PF_2 whose parameters (Table I) were consistent with those of Nelson, Jackel, and Gordy. Unfortunately our[1,2] previous identifications of the radical appear to have been incorrect. It would appear that Wei, Current, and Gendell[3] had also detected PF_2, although it was probably incompletely frozen into the matrix. Specifically, we feel that their "perpendicular" features might well be due to freely rotating radicals, suggesting the following isotropic parameters for PF_2 in an argon matrix, $g = 1.9922$, $a_P = 83.0$ G, and $a_F = 33.5$ G.

Wan, Morton, and Bernstein's radical is almost certainly PO_2F_2. It has already been shown[8] that NH_4PF_6 is susceptible to hydrolysis, and doubtless some conversion to $ND_4PO_2F_2$ occurred during the deuteration procedure. Furthermore, Begum, Subramanian, and Symons[9] have reported parameters for PO_2F_2 ($g = 2.0100$, $a_P = 43.8$ G, and $a_F = 52.5$ G) which are similar to those of the radical detected[2] in irradiated ND_4PF_6.

The radical labelled PF_2 by Fessenden and Schuler[1] must also be reidentified. Since its spectrum can be observed when pure[10] SF_6 is irradiated, it must arise from a sulfur-centered radical, now believed to be SF_3. The spectrum of SF_3 is considerably enhanced by certain additives, notably PF_3. For example, the intensity of the published spectrum[1] (1% PF_3 in SF_6) is approximately ten times stronger (relative to that[11] of SF_5) than that observed in irradiated pure SF_6. The PF_3 seems either to participate in reactions involving SF_3 or to modify the matrix to make stabilization of SF_3 more likely.

The radical SF_3 is the prototype of certain sulfanyl radicals which have recently been studied.[12] These radicals, of the general type $(R_fO)_3S$, where $R_f = CF_3$ or SF_5, possess two equivalent ligands whose (^{19}F) hyperfine interactions exceed those of the unique ligand. In other words these derivatives of SF_3 do not possess a threefold axis, but a plane of symmetry. Consequently one would also expect SF_3 to exhibit a spectrum showing hyperfine interactions with two equivalent ^{19}F nuclei, and a somewhat smaller interaction with a unique ^{19}F nucleus. The parameters in Table II a, which were obtained from the aforementioned spectrum, accord very well with these deductions.

We have also succeeded in observing the spectrum of SF_3 in the liquid phase, by photolyzing a solution[13] of H_2S or D_2S and CF_3OF in Freon 13 at −110 °C. The spectrum of SF_3, whose parameters appear in Table II b, persisted for only a few minutes. It is curious to note that the hyperfine interaction of the two equivalent ^{19}F nuclei is slightly less in solution than in an SF_6 matrix, presumably the result of a slight change in the radical geometry.

TABLE I. ESR parameters of PF_2 in (a) C_2F_6 matrix at −140 °C and (b) in PF_2Cl dissolved in Freon 13 at −100 °C.

	(a)	(b)
g	1.9994 ± 0.0003	1.9997 ± 0.0001
a_P	81.3 ± 0.2 G	82.0 ± 0.1 G
a_F	33.1 ± 0.2 G	32.4 ± 0.1 G

TABLE II. ESR parameters of SF_3 in (a) SF_6 matrix at −135 °C and (b) Freon 13 at −110 °C.

	(a)	(b)
g	2.0054 ± 0.0001	2.0050 ± 0.0001
a_F(one nucleus)	40.4 ± 0.1 G	41.0 ± 0.1 G
a_F(two nuclei)	54.3 ± 0.1 G	48.7 ± 0.1 G

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[4]W. Nelson, G. Jackel, and W. Gordy, J. Chem. Phys. 52, 4572 (1970).
[5]The experimental technique was similar to that described in Ref. 1. Solid C_2F_6 (m.p. −94 °C) allows free rotation of small radicals down to about −165 °C as shown by the isotropic spectra observed for CF_3 and C_2F_5 in this matrix (R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 43, 2704 (1965) and in *Advances in Radiation Chemistry*, edited by M. Burton and J. L. Magee (Wiley-Interscience, New York, 1970), Vol. 2, p. 90.
[6]In addition to the ESR lines of PF_2 there were lines of PF_4 (the same spectrum as in SF_6[1]) and weak lines of C_2F_5.
[7]J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorganic Syntheses*, edited by E. L. Muetterties (McGraw-Hill, New York, 1967), Vol. 10, p. 153.
[8]R. W. Fessenden, J. Mag. Res. 1, 277 (1969).
[9]A. Begum, S. Subramanian, and M. C. R. Symons, J. Chem. Soc. A 1970, 1323.
[10]Mass spectroscopic analysis of the SF_6 used in that work shows CF_4 to be the only significant impurity (~1%) and that PF_3 cannot be present to over about 0.01 mole%.
[11]This spectrum was originally assigned by Fessenden and Schuler[1] to SF_4^+. See J. R. Morton and K. F. Preston, Chem. Phys. Lett. 18, 98 (1973) for the present assignment.
[12]J. R. Morton and K. F. Preston, J. Phys. Chem. 77, 2645 (1973).
[13]10μl each of liquid H_2S and CF_3OF, separated by 100μl of Freon 13, were allowed to warm up to −96 °C. If the sample did not explode, the spectrum of SF_3 could be detected upon photolysis at −110 °C.